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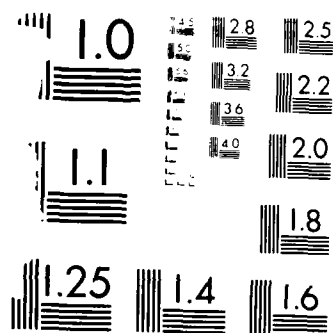
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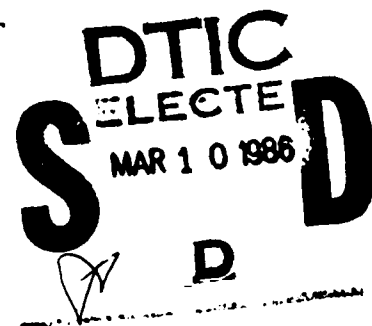
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  — This investigation was motivated in part by the observation that the empirical pseudopotential calculations of the TiC electronic structure produced valence electron densities that disagree severely with those obtained from first-principles calculations. The intent of this study was to see if the mixed-basis band structure interpolation scheme (MBBSIS) could be used to obtain reliable band structures and charge densities for more complex systems, such as TiC, TiN, and TiO.		

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Running Title: Summary Abstract: Analysis of chemical bonding

**Summary Abstract: Analysis of chemical bonding in TiC, TiN, and TiO using second-principles band structures from photoemission data**

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(Received 16 September 1985; accepted 30 September 1985)

This investigation was motivated in part by the observation that the empirical pseudopotential calculations<sup>1</sup> of the TiC electronic structure produced valence electron densities that disagree severely with those obtained from first-principles calculations.<sup>2</sup> The intent of this study was to see if the mixed-basis band structure interpolation scheme (MBBSIS)<sup>3</sup> could be used to obtain reliable band structures and charge densities for more complex systems, such as TiC, TiN, and TiO.

Our method of calculation has been described in detail elsewhere.<sup>4</sup> The electron density associated with each band state was defined as the square of its MBBSIS eigenfunction, which is a combination of 39 orthogonalized plane waves (OPW) and 5 *d*-wave functions in the present scheme.

In a recent study, detailed band mapping was performed using angle-resolved photoelectron spectroscopy (ARPES) to obtain band dispersions for TiC<sup>5</sup> and TiN.<sup>6</sup> Noticeable discrepancies between the first-principles results<sup>5,6</sup> and ARPES data<sup>5,6</sup> can be found. In particular, the experimental bands have a clear band gap in the valence bands that does not appear in the calculations.<sup>6</sup> The MBBSIS energy bands were empirically adjusted for TiC and TiN, and agree very well with the ARPES data.<sup>5,6</sup>

The total valence electron densities of TiC, TiN, and TiO calculated by the MBBSIS fitted to the first-principles results agree very well with the densities calculated in Ref. 2. The electron densities around the nonmetal atoms are spherically symmetric and show increased localization going from TiC to TiO. The electron densities around the titanium atom strongly deviate from spherical symmetry, and the deviation changes from  $e_g$  symmetry for TiC to  $t_{2g}$  symmetry for TiO. The relationship between banding and bonding may be illustrated by examining states with *k* points along the  $\Delta$  direction. The electron density plots for the first band with  $\Delta_1$  symmetry for the three Ti compounds illustrate the covalent bonding ( $pd_\sigma$ ) between nonmetal 2*p* and Ti  $t_{2g}$  orbitals. The electron densities around the Ti atom are reduced going from TiC to TiO, while those around the nonmetal atoms increase. This indicates that TiC exhibits the highest degree of covalent bonding and that the more ionic character increases as the series progresses from TiC to TiO. Similar features are also found in the electron densities of the second band of  $\Delta_1$  symmetry. The covalent bonding ( $pd_\sigma$ ) character between the nonmetal 2*p* and Ti  $e_g$  orbitals is decreased going from TiC to TiO. The electron density plot for the band of  $\Delta_2$  symmetry shows metal-metal ( $dd_\sigma$ ) bonding. Most of electron density is piled up around the Ti atoms and the minimum electron densities are found around nonmetal atoms. Figure 1 presents both (a) the total charge density of the bands fitted to the first-principles results and (b) that of the empirically adjusted bands for TiN. The latter plot shows a higher electron density at the C atom and a lower electron density at the Ti atom than the former. In TiC, contrary to the TiN result, the corresponding plot of the semiempirical charge density shows a higher concentration at the Ti atom and a lower electron density at the C atom than those of the first-principles results. This means that the semiempirical band structures indicate more covalent bonding character in TiC and more ionic in TiN than the first-principles results indicate.

In summary, the contribution of covalent, ionic, and metallic bonding in the three Ti compounds may be visualized in the charge densities calculated by the MBBSIS.

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<sup>2</sup>P. Blaha and K. Schwartz, *Int. J. Quantum Chem.* 23, 1535 (1983).

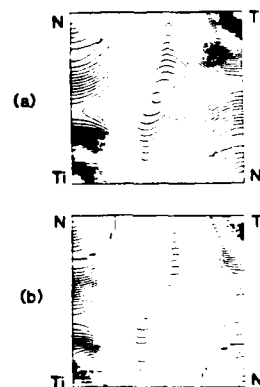
<sup>3</sup>R. L. Benbow and N. V. Smith, *Phys. Rev. B* 27, 3144 (1983).

<sup>4</sup>S. Kim and R. S. Williams, *to be published*.

<sup>5</sup>A. Callenias, L. I. Johansson, A. N. Christensen, K. Schwartz, and J. Redinger, *Phys. Rev. B* 27, 5934 (1983).

<sup>6</sup>L. I. Johansson, A. Callenias, P. M. Stefan, A. N. Christensen, and K. Schwartz, *Phys. Rev. B* 24, 1883 (1981).

FIG. 1. Comparison of contour plots between (a) the total charge density of the bands fitted to the first-principles results of Ref. 6 and (b) that of the empirically adjusted bands for TiN, normalized to 9 electrons per unit cell. The projection shown is a (100) plane bounded by two Ti and N atoms.



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